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Atmospheric Acidification Chemistry: A Review

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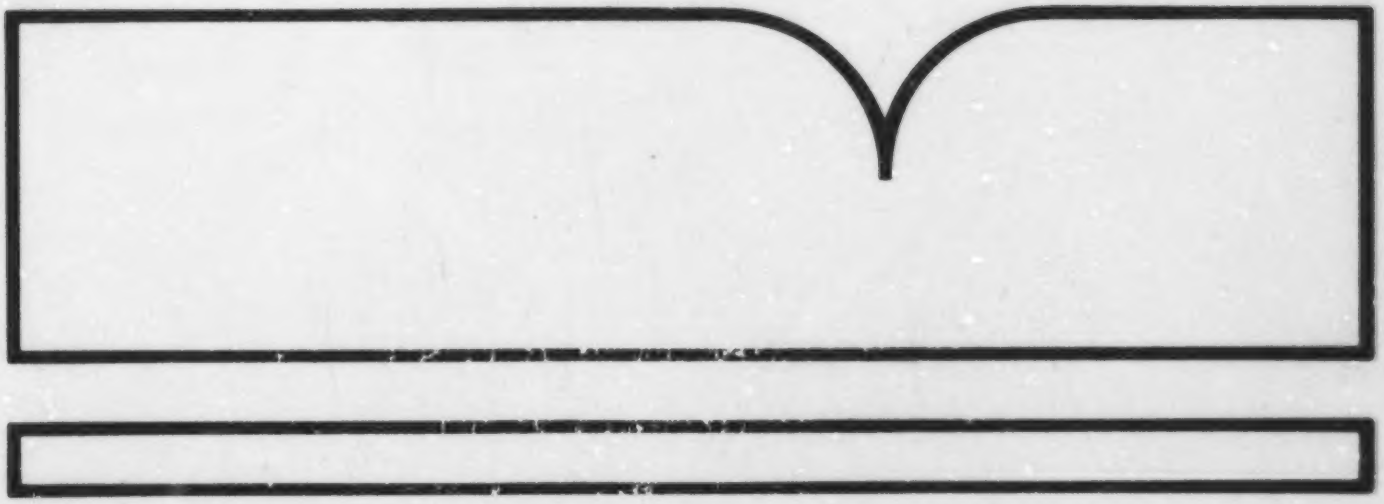

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ATMOSPHERIC ACIDIFICATION CHEMISTRY: A REVIEW

BY

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16. ABSTRACT

Atmospheric acidification is the result of the oxidation of sulfur, nitrogen, and organic compounds to form their corresponding acids. The gasand aqueous-phase pathways depend on the production of oxidizing free radicals (HO, CH_3O_2) that react directly with these compounds or produce molecular oxidants. The most important molecular oxidants are H_2O_2, organic peroxides, and O_3. Except for O_3-olefin reactions, these molecular oxidants are not reactive in the gas phase, but they are highly reactive in the aqueous phase with dissolved reductants (SO_2, HNO_2, organics). Thus, the molecular oxidants may be generated in a photochemically active region and transported long distances before reacting with dissolved reductants in the aqueous phase, such as fogs, clouds, and rain. Changes in H_2SO_4 and HNO_3 atmospheric production rates are expected to be a function of changes in the emission rates of SO_2, NO_x, and VOC. A reduction in emission rate of SO_2 will lead to a reduction in gas-phase production of H_2SO_4. However, if SO_2 concentration exceeds that of H_2O_2 reduction in SO_2 emissions may not lead to a reduction in aqueous-phase production of H_2SO_4. Effective control of H_2O_2 production is dependent on scientific advances to determine its formation mechanisms and rates.

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ABSTRACT

Atmospheric acidification is the result of the oxidation of sulfur, nitrogen, and organic compounds to form their corresponding acids. The gas- and aqueous-phase pathways depend on the production of oxidizing free radicals (HO, CH_3O_2) that react directly with these compounds or produce molecular oxidants. The most important molecular oxidants are H_2O_2, organic peroxides, and O_3. Except for O_3-olefin reactions, these molecular oxidants are not reactive in the gas phase, but they are highly reactive in the aqueous phase with dissolved reductants (SO_2, HNO_2, organics). Thus, the molecular oxidants may be generated in a photochemically active region and transported long distances before reacting with dissolved reductants in the aqueous phase, such as fogs, clouds, and rain. Changes in H_2SO_4 and HNO_3 atmospheric production rates are expected to be a function of changes in the emission rates of SO_2, NO_x, and VOC. A reduction in emission rate of SO_2 will lead to a reduction in gas-phase production of H_2SO_4. However, if SO_2 concentration exceeds that of H_2O_2, reduction in SO_2 emissions may not lead to a reduction in aqueous-phase production of H_2SO_4. Effective control of H_2O_2 production is dependent on scientific advances to determine its formation mechanisms and rates.

INTRODUCTION

Increases in environmental acidification result from the oxidation of sulfur, nitrogen, and carbon compounds to form the strong mineral acids H_2SO_4 and HNO_3 and organic acids (Work Group 2, 1982). The principal paths of atmospheric acidification are reactions among pollutants in the gas phase, in or on particles, and in the aqueous phase. Ecosystem acidification occurs through the wet and dry deposition of these acids. Also, the wet and dry deposition of acidic precursors and oxidants may lead to acidifying reactions in terrestrial and aquatic ecosystems. Presently it is not possible to formulate a set of mathematical expressions to describe completely the source/receptor pathways, which are shown in Fig. 1. Meteorological processes and complex chemical processes can be formulated, but there are important deficiencies in knowledge in both. This review will focus on the chemistry of acidification. Conclusions and possible general control options shall be stated, but with the recognition that the distribution of anthropogenic sources, contribution of natural sources, and meteorology are important and cannot be dismissed.

ACIDIFICATION PATHWAYS

The chemical paths leading to the acidification of the atmosphere depend on the production of oxidizing free radicals. The oxidizing free radicals may react directly with SO_2, NO_2, and organic compounds to yield H_2SO_4, HNO_3, and carboxylic acids, or they may react to produce molecular oxidants. The lifetime of the strongly oxidizing free radicals in the atmosphere is less than 1 second, so their transport distance in the atmosphere is less than several meters, which is insignificant. The most important molecular oxidants that are produced are hydrogen peroxide (H_2O_2), organic peroxides, ozone (O_3), and perhaps nitrogen dioxide (NO_2), nitrous acid (HNO_2), dinitrogen

trioxide (N_2O_3. Ozone may react directly in the gas phase with olefinic organic pollutants to produce carboxylic acids, but in general, the molecular oxidant reactions with SO_2 and NO_2 are unimportant for atmospheric acidification. However, they are important for dissolved SO_2, HNO_2, and perhaps organics in the aqueous phase. Thus, the molecular oxidants may be generated in a photochemically active region and transported long distances (greater than 1000 km) before reacting with acid precursor gases in the aqueous phase (clouds, rain, or ecosystem) to produce the acids.

Photochemical Oxidation Cycle

Free radical attack on atmospheric volatile organic compounds (VOC) is initiatated by a select group of compounds which are for the most part activated by sunlight. Formaldehyde (CH_2O) and HNO_2 photolyses show high potential as free radical initiators during the early morning sunrise period. The free radical attack causes the VOCs to decompose by various paths resulting in the production of the oxidizing free radicals HO (hydroxy), HO_2 (hydroperoxy), RO (alkoxy), RO_2 (alkylperoxy) and partially oxidized products which may also be photoactive radical-producing compounds. The RO_2 radicals react with NO, converting it to NO_2, and in the process produce HO and RO radicals. RO radicals can be further oxdized, forming additional RO_2 radicals and partially oxidized products, thereby completing the inner cyclical loop reaction process illustrated in Fig. 2; or they may attack the VOC pool (this is the major path for producing HO) present in the atmosphere, thereby completing the outer loop reaction process. The resultant effect in either case is the conversion of NO to NO_2 with a commensurate oxidation of reactive organic carbon to form the oxidation products CO_2 and H_2O. The complex mixture of organic compounds present in the polluted atmosphere react with initiator radicals at different rates dependent upon their molecular structure, the result being varying yields of free radical species, O_3, NO_2, H_2O_2,

peroxyacetyl nitrate (PAN), and other partially oxidized organic products as a function of VOC composition and [VOC] and [NO_x]. For a more detailed discussion of the oxidant chemistry of polluted atmospheres, see Calvert (1983), Durham et al. (1982), and their references.

HO radical reactions seem to be the dominant gas-phase mechanism by which carbon monoxide, hydrocarbons, nitrogen dioxide and sulfur dioxide are consumed in the atmosphere (Niki et al., 1972; Demerjian et al., 1974; Calvert et al., 1978). HO is a highly reactive transient species, which contrary to its organic free radical conterparts, shows limited variations in concentration with changes in atmospheric [VOC] and [NO_x] levels, a result readily explainable upon consideration of the free radical production and consumption sources. In the case of HO radical, ambient conditions which enhance its production tend also to consume the radical at an equivalent rate. The result is a faster cycling in the VOC-NO_x oxidation but very little perturbation in the HO steady state concentration. Under similar conditions an enhanced production of organic free radicals, mainly RO_2, is not offset by an increased consumption, and this results in increased steady state concentrations. Hence, the concentration of the organic free radicals is subject to variations due to changes in VOC and NO_x levels, in contrast to the HO concentration.

Gas-Phase Acidification Reactions

Calvert and Stockwell (1984) have reviewed current rate constant data for SO_2 reactions with free radicals and have concluded that the HO radical dominates the rate of SO_2 oxidation in the clean and polluted lower troposphere.

$SO_2 + HO \rightarrow H_2SO_4$ (unbalanced) (1)

Typical average rates of SO_2 oxidation at mid-northern latitudes were estimated to be 16%/24-h period for summer and 3%/24-h period for winter. The alkyl peroxyl radicals (especially CH_3O_2) and ozone-alkene Crigree intermediates may make important contributions to the gas-phase oxidation of SO_2 during periods of elevated $[NO_x]$ and [VOC].

NO_2 gas-phase oxidation in the lower troposphere is also likely dominated by HO radical reaction.

$$NO_2 + HO \dashrightarrow HNO_3 \qquad (2)$$

For the same conditions as for SO_2, the NO_2 oxidation rate is 150%/24-h period for summer and 25%/24-h period for winter (Calvert and Stockwell. 1984).

The known features of the gas-phase oxidation of SO_2 and NO_2 in the lower troposphere are presented in Table 1. The rates are bimolecular concentration functions. They are first-order in $[SO_2]$ or $[NO_2]$, but they may not be linear on a regional transport scale. That is

$$d[H_2SO_4]/dt = -d[SO_2]/dt \neq (\text{constant})[SO_2] \qquad (3)$$

$$d[HNO_3]/dt = -d[NO_2]/dt \neq (\text{constant})[NO_2]. \qquad (4)$$

The non-linearity in the rates is due to: (a) the variation of [HO] as a function sunlight intensity, and to some extent, [VOC], $[NO_x]$, and $[H_2O]$, and (b) the variations of $[CH_3O_2]$ and $[RO_2]$ are complex functions that depend strongly on sunlight intensity, the ratio $[VOC]/[NO_x]$, and [VOC]. Thus, the rate functions for the gas phase oxidation of SO_2 may be highly variable. It has not been demonstrated that they may be represented by a 24-h average rate for transport/transformation/deposition modeling over transport time scales

of several days. Because the atmospheric life-times of the free radicals HO and CH_3O_2 are less than 1 s, they cannot be transported for scale lengths greater than several meters.

The gas-phase oxidation of volatile organic compounds is known to occur through reaction with free radicals, and in the case of olefins, with O_3. Other reaction paths are not established, but aqueous pathways may also be important.

Aqueous-Phase Acidification Reactions

The relative magnitudes of the contribution of gas-phase and aqueous-phase formation of H_2SO_4 are not established but expected to vary as a function of season. At southern latitudes for all seasons, it is likely that the gas-phase reaction

$$SO_2 + HO \text{ --> } H_2SO_4 \quad \text{(unbalanced)} \qquad (1)$$

is an important acidification pathway. At southern and northern latitudes for all seasons, it is likely that the aqueous reactions are important and in the winter dominate the gas-phase pathway for northern latitudes. The aqueous-phase reactions thought to be the most important are (Work Group 2, 1982):

$$SO_{2(g)} + H_2O_{(liq)} \text{ <--> } SO_2 \cdot H_2O \qquad (5)$$

$$SO_2 \cdot H_2O \text{ <--> } H^+ + HSO_3^- \qquad (6)$$

$$HSO_3^- + H_2O_2 \text{ --> } H^+ + SO_4^{2-} + H_2O \qquad (7)$$

$$HSO_3^- + O_3 \text{ --> } H^+ + SO_4^{2-} \quad \text{(unbalanced)} \qquad (8)$$

$$HSO_3^- + NO_2^- \text{ --> } H^+ + SO_4^{2-} \quad \text{(unbalanced)} \qquad (9)$$

$$HSO_3^- + O_2 \xrightarrow{Mn(II)} H^+ + SO_4^{2-} \quad \text{(unbalanced)} \qquad (10)$$

$$HSO_3^- + O_2 \xrightarrow{Fe(III)} H^+ + SO_4^{2-} \quad \text{(unbalanced)} \qquad (11)$$

$$HSO_3^- + O_2 \xrightarrow{C(O)} H^+ + SO_4^{2-} \quad \text{(unbalanced)} \qquad (12)$$

At this time, the importance of the aqueous path for NO_2 oxidation to HNO_3 is not known, but it may be significant. The knowledge of aqueous oxidation rates of dissolved SO_2 is barely adequate for simple clean systems, inadequate for NO_x and N-oxy acids systems, and practically non-existent for complex sulfur dioxide/N-oxides/N-oxy acid/organic/catalyst/oxidizer systems. Studies of these polluted air-aqueous systems are made difficult by the lack of high-purity reagents, the lack of sensitive instrumentation/methods to determine the reaction rates at ambient pollutant concentrations, and mass transfer rate limitations of practical bulk gas-liquid contact chemical reactors (Durham et al., 1982).

The dissolved SO_2 oxidation rate expressions for reactions thought to be important are shown in Table 2 for H_2O_2, O_3, NO_2, HNO_2, and catalysts. All of the rates are a function of the liquid water content (LWC) of the atmosphere, except for carbon, C(O). These rates have been expressed in terms of the concentration of $SO_2 \cdot H_2O$, often referred to as "sulfurous acid," which is directly related by Henry's Law constant (H_L) to the gas-phase concentration of SO_2:

$$[SO_{2(g)}] = H_L[SO_2 \cdot H_2O] \tag{13}$$

In similar fashion, the aqueous phase concentrations of H_2O_2, O_3, and HNO_2 are directly related by their H_Ls to their gas-phase concentrations. Thus, a change in the gas-phase concentration of any of these species has a direct effect on the rate expression in Table 2. Since the concentrations of the dissolved oxidants and LWC are are expected to be highly variable, none of the reaction rates are likely to be adequately represented over a regional scale by a linear rate equation. That is,

$$\text{rate of } H_2SO_4 \text{ formation} \neq k_a[SO_2]. \tag{14}$$

The oxidation rate of dissolved SO_2 by H_2O_2 possesses an important feature. When the rate is expressed formally as in Table 2 in terms of $[SO_2 \cdot H_2O]$ instead of $[HSO_3^-]$, the aqueous rate is dependent on the gas-phase concentrations of SO_2 and H_2O_2 and is independent of $[H^+]$ over the pH range 2-6 (Martin and Damschen, 1981). Thus, as the solution becomes more acidic, the rate of acid formation does not decrease. Since the SO_2 oxidation rate by H_2O_2 is fast, the acidification of the aqueous phase can be considered in terms of the "limiting" and the "excess" reactants. Such systems will continue to react until the "limiting" reactant is totally consumed. The concentration of the "excess" reactant does not significantly influence the amount of acid that is formed. In terms of total conversion, the system is "linear" with respect to the limiting reactant, and "non-linear" with respect to the "excess" reactant.

The oxidation rate of dissolved SO_2 by O_3 may be expressed formally as in Table 2 in terms of $[SO_2 \cdot H_2O]$ instead of $[HSO_3^-]$, and it is dependent on the gas-phase concentrations of SO_2 and O_3 and on $[H^+]^{-1}$. Therefore, the rate will respond directly to changes in gas-phase SO_2 and O_3, but more importantly, as the aqueous solution acidity increases, the oxidation (acidification) rate decreases. For pH less than about 6 and gas-phase $[O_3]$ = 50 ppb, this reaction is not as effective as the H_2O_2 oxidation at gas-phase concentrations greater than 1 ppb (Durham et al., 1984; Penkett et al., 1979). In terms of total system conversion, the O_3 oxidation should be regarded as "non-linear." For pH below about 5, the conversion in clouds and rain is unimportant for likely concentration ranges in regional air for SO_2 (5-20 ppb) and O_3 (40-80 ppb).

The oxidation of dissolved SO_2 is not important for the concentrations of NO and NO_2 usually found in the atmosphere (Lee and Schwartz, 1981). These gases are relatively insoluble in water. Their atmospheric concentrations

are too low to form appreciable concentrations of reactive and soluble species such as N_2O_3 and N_2O_4, and modeling of sub-cloud scavenging has demonstrated that they do not compete with H_2O_2 and O_3 in the acidification of raindrops (Durham et al., 1981). However, NO and NO_2 may be important aqueous-phase oxidants near their strong point sources.

Dissolved SO_2 may be oxidized by HNO_2, Mn(II), Fe(III), and C(O). However, modeling calculations (Durham et al., 1981; Durham et al., 1984) indicate that these reactions for a sub-cloud scavenging event are not competitive with those of H_2O_2 and O_3. Therefore, reactions 9 through 12 are likely to be important only in special circumstances, such as near point sources or, perhaps in the absence of H_2O_2 and O_3.

The major pathways of atmospheric acidification are summarized in Figure 3. In the gas phase, the main oxidants are the free radicals HO, CH_3O_2, and perhaps the Crigee intermediate and other free radicals. These reactions require the estabishment of the photochemical cycle shown in Figure 2. The photochemical cycle also leads to the formation of the molecular oxidants, especially H_2O_2, organic peroxides, and O_3. These oxidants are not effective in the gas phase for the oxidation of SO_2, but are in the aqueous phase, such as atmospheric aqueous aerosol, cloud and fog droplets, and raindrops, and surface waters.

ATMOSPHERIC OBSERVATIONS

A two-dimensional reactive scavenging model has been evaluated against the data of a single storm event for three SO_2 oxidation schemes: (a) aqueous-phase oxidation by dissolved O_3, (b) aqueous-phase oxidation by dissolved H_2O_2, and (c) pseudo first order aqueous oxidation at a rate proportional to dissolved S(IV) concentration (Easter and Hales, 1983). Aerosol scavenging was included in each scheme. Best agreement between the model and the

experimental data was obtained for a combination of oxidation by H_2O_2 and O_3, with aerosol scavenging. It appears that H_2O_2 dominates the oxidation of SO_2, and O_3 does not contribute substantially to the acidification until the H_2O_2 has been consumed. This result is also consistent with reactive sub-cloud scavenging modeling (Durham et al., 1984).

Summer and winter observations of cloud air and chemical quality have been made at Whiteface Mountain (McLaren et al., 1984; Camarota et al., 1983; Galvin et al., 1983). The summer time observations indicate that SO_2 is rapidly and completely oxidized in clouds, due to H_2O_2 aqueous concentrations in the range 800-2000 ppb. The winter time observations are entirely different. SO_2 is apparently not oxidized in the cloud at Whiteface, and H_2O_2 is not present.

REDUCTION OF ATMOSPHERIC ACIDIFICATION

Effective options shown in Table 3 for the reduction of atmospheric acidification must take into account the response of H_2SO_4, HNO_3, and organic acid production as a function of SO_2, NO_x, and VOC emission reductions. The task of formulating options is difficult due to the lack of knowledge of the relative contribution of gas-phase and of aqueous-phase pathways for forming the acids. The H_2SO_4 production is the case best understood, but the relative contribution of the main gas-phase reaction (HO oxidation of SO_2) is not established. The rate of H_2SO_4 gas-phase production may be reduced by reducing the concentration of oxidizing free radicals (HO, CH_3O_2), or SO_2, or both. Reduction of [HO] is not practical; it is produced in the photochemical oxidant cycle and its concentration is not very sensitive to changes in precursor (NO_x and VOC concentrations. Also, this reaction is unimportant in locations where the photochemical oxidant cycle is not established, such as latitudes greater than about 35°N from late Fall to early Spring.

The H_2O_2 oxidation of dissolved SO_2 in cloud and rain droplets is likely the dominating H_2SO_4 production reaction for all seasons and locations. Considered in terms of the "limiting reactant", H_2SO_4 aqueous-phase production will be responsive to control of SO_2 or H_2O_2, depending on which is present at the lower concentration. During non-photochemical conditions, (e.g., the Northeastern U.S. in the winter months), the oxidants H_2O_2 and O_3 are not formed locally, but they may be transported from production regions at southerly latitudes. In such a case, oxidants would be the "limiting reactants" (which is consistent with observations at Whiteface Mountin), and control of SO_2 emissions to reduce H_2SO_4 aqueous-phase production will not be effective. In regions that are photochemically active, the oxidants may be present at concentrations that exceed those of SO_2. Effective reduction of H_2SO_4 production in that case will require SO_2 reduction.

Reduction in oxidant production (to reduce its contribution to aqueous-phase acidification) poses difficult problems. H_2O_2, and perhaps organic peroxides, are regarded as the main aqueous oxidizers of SO_2. However, their atmospheric formation mechanisms are not established. If their production is related to O_3 production, the control of H_2O_2 poses difficult problems. It would be necessary to reduce VOC emissions (and perhaps NO_x emissions) in such a manner that $[VOC]/[NO_x]$ is reduced in the photochemically active regions. However, at this time, the degree of source control to achieve reduction in H_2O_2 production cannot be specified and is the object of a major research program (NAPAP, 1984). It is expected that reductions in acidic deposition to specific locations will require strategies that include SO_2, NO_x, and VOC emission reductions as a function of source location and season.

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TABLE 1. Features of Gas-Phase SO_2 and NO_2 Oxidation in the Troposphere.

	Free Radical Oxidizer	Rate function: $-d[SO_2]/dt = d[H_2SO_4]/dt =$	Linear 24-hr Average Rate?[1]	Oxidizer Transported on Regional Scale?
a.	HO	$k_a[SO_2][HO]$	No	No
b.	RO_2	$k_b[SO_2][RO_2]$	No	No
c.	HO	$k_c[NO_2][HO]$	No	No

[1]Can overall rate of disappearance of SO_2 be expressed as: $-d[SO_2]/dt =$ (constant)$[SO_2]$?

TABLE 2. Features of Aqueous Phase SO_2 Oxidation in the Lower Troposphere.

	Molecular Oxidizer	Rate function: $-(LWC)^{-1}d[SO_2 \cdot H_2O]/dt =$ $(LWC)^{-1}d[H_2SO_4]/dt =$	Linear 24-hr Average Rate?[1]	Oxidizer Transported on Regional Scale?
d.	H_2O_2	$k_d[H_2O_2][SO_2 \cdot H_2O]$	No	Yes
e.	O_3	$k_e[O_3][SO_2 \cdot H_2O]/[H^+]$	No	Yes
f.	HNO_2	$k_f[HNO_2][SO_2 \cdot H_2O]/[H^+]^2$	No	Yes
g.	Mn(II)	$k_g[Mn(II)]$	?	Yes
h.	Fe(III)	$k_h[Fe(III)][SO_2 \cdot H_2O]/[H^+]$	?	Yes
i.	C(O)	$(LWC)^{-1}k_i[C(O)]$	?	Yes

[1]Can overall rate of disappearance of SO_2 be expressed as: $-d[SO_2 \cdot H_2O]/dt =$ (constant)$[SO_2]$?

TABLE 3. Change in Local H_2SO_4 Atmospheric Formation Rates Due to Decrease in Concentration of Pollutants.

Oxidizer	Decrease in Rate as a Function of Decrease in: $[SO_2]$	Decrease in Rate as a Function of Decrease in: [Oxidizer]
Gas Phase:		
Free radicals	linear	(impractical)
Aqueous Phase:		
H_2O_2		
$<[SO_2]$	non-linear[a,b]	linear
$>[SO_2]$	linear	non-linear[a,b]
O_3		
$<[SO_2]$	non-linear[a,c]	non-linear[a,c]
$>[SO_2]$	non-linear[a,c]	non-linear[a,c]

[a]The rate of H_2SO_4 formation is: $d[H_2SO_4] < (\text{constant})[SO_2]$.
[b]Due to consumption of limiting reactant.
[c]Due to H^+ inhibition.

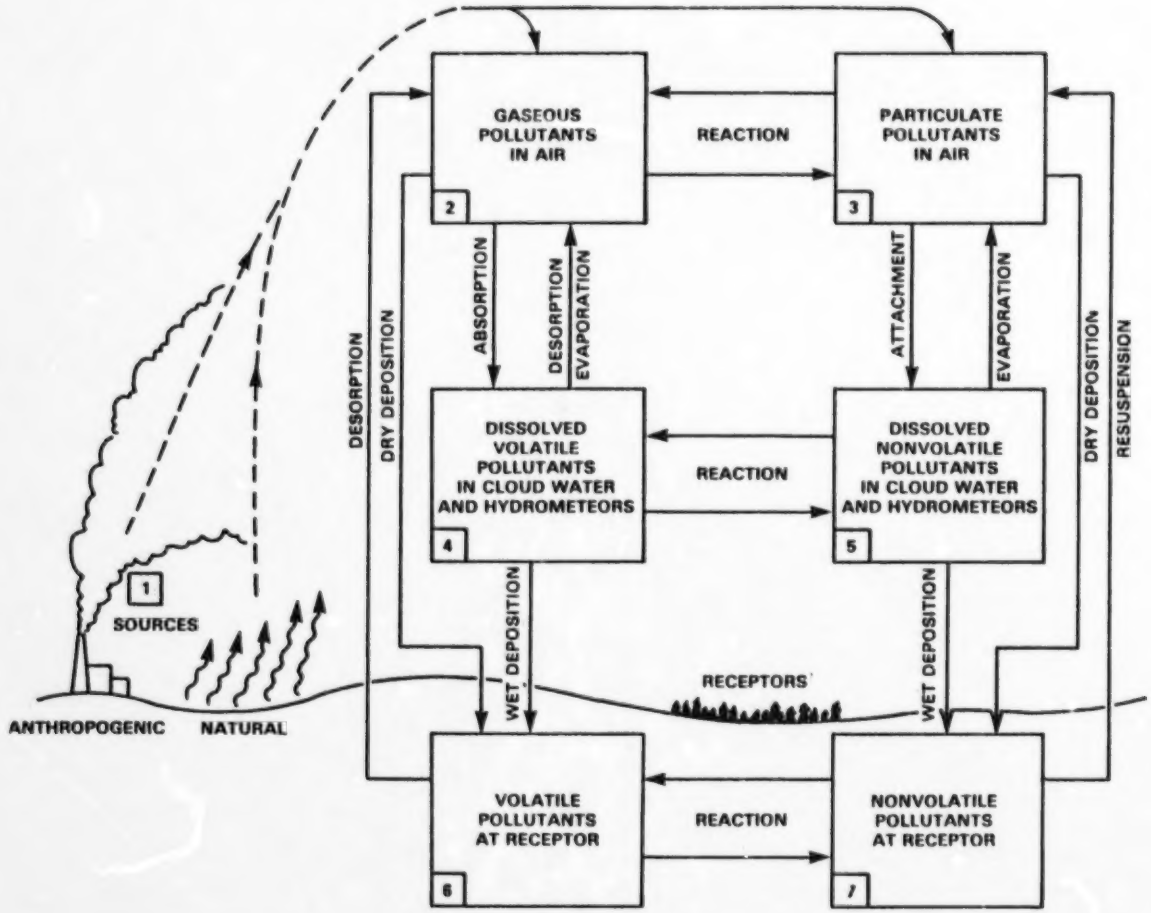

Figure 1. Simplified schematic of pollutant chemical transformation, scavenging, and deposition pathways between sources and receptors. This diagram does not illustrate other important processes and factors affecting acidification, such as meteorological transport and source emission type and distribution.

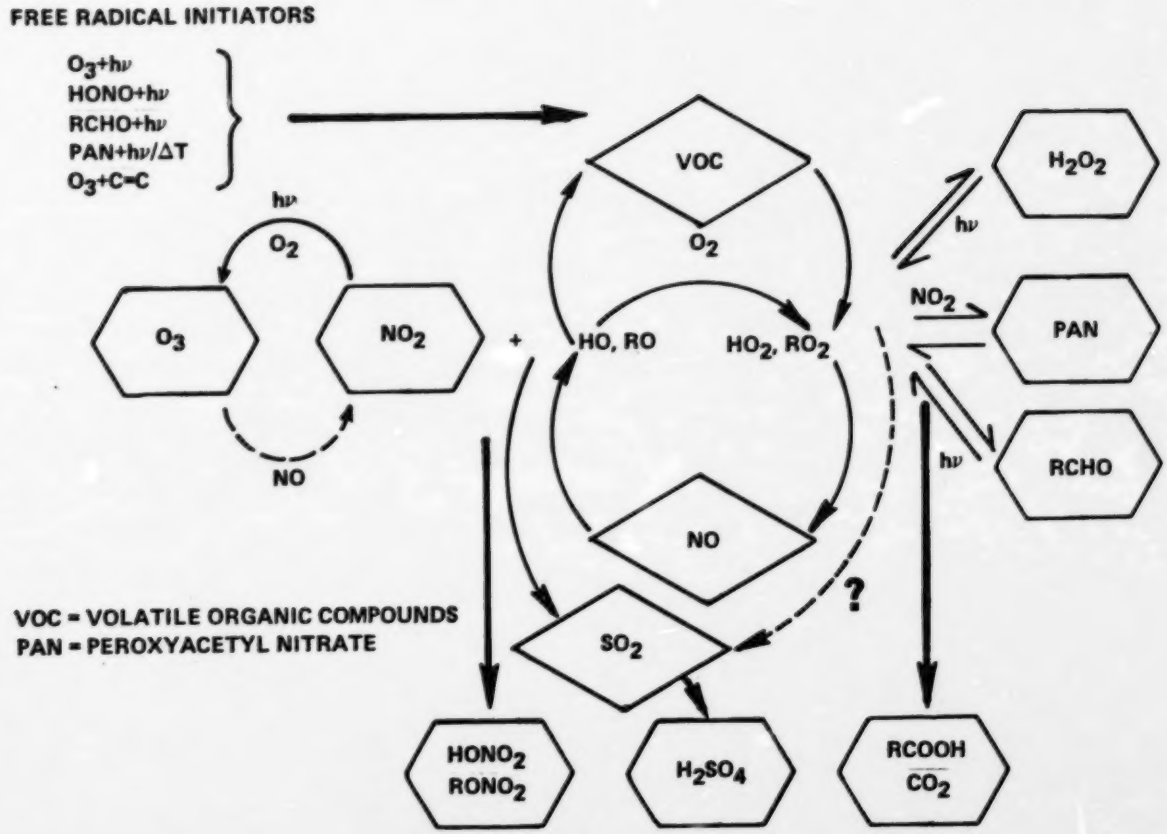

Figure 2. Schematic of the polluted atmospheric photo-oxidation cycle. Pollutants emitted from anthropogenic sources are shown in diamond boxes; pollutants formed in the atmosphere are shown in hexagonal boxes. The reaction scheme represents gas-phase chemistry only.

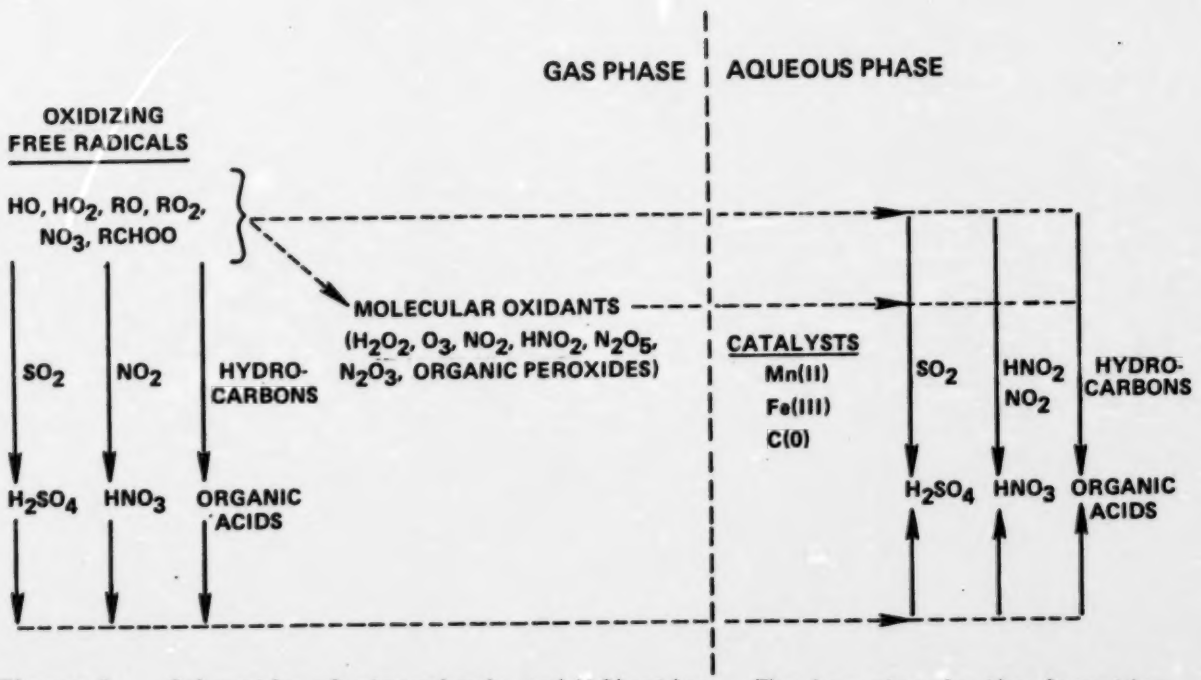

Figure 3. Schematic of atmospheric acidification. The key step is the formation of the oxidizing free radicals, which may either oxidize directly SO_2, NO_2, and hydrocarbons to their corresponding acids or may form the molecular oxidants. The molecular oxidants may be transported long distances, dissolve in the aqueous phase in fogs, clouds, or rain, and oxidize dissolved SO_2, HNO_2, NO_2, and organics.